

PRODUCTION OF ALIPHATIC FLUOROCARBONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to processes for the production of aliphatic fluorocarbons.

2. Description of Related Art

Aliphatic fluorocarbons are a group of chemicals that range from inert, highly stable substances to reactive unsaturated fluorocarbons. As used throughout this disclosure and in the claims, the term "aliphatic fluorocarbon" is defined as an aliphatic compound which has carbon to fluorine bonds, and which may also contain hydrogen and chlorine. Aliphatic fluorocarbons may range from compounds having only single bonds to those having multiple bonds. The single bond compounds are frequently inert and nonflammable. These are useful as inert solvents, lubricants, and blowing agents as examples. Fluorocarbons having double bonds, fluoroolefins, are very reactive species useful in the production of a variety of chemicals and specialty polymers. Fluorocarbons having triple bonds are also very reactive. Methods of manufacturing these groups of chemicals efficiently are always of interest to the chemical industry.

SUMMARY OF THE INVENTION

The present invention relates to a new manufacturing process for preparing a desired aliphatic fluorocarbon product comprising the following steps:

- a) subjecting an aliphatic fluorocarbon starting compound to a treatment which will break at least one chemical bond of the aliphatic fluorocarbon starting compound to form a reactive aliphatic fluorocarbon intermediate compound;
- b) reacting the reactive aliphatic fluorocarbon intermediate compound with another reactive compound to yield the desired aliphatic fluorocarbon product and an undesired aliphatic fluorocarbon product;
- c) separating said desired aliphatic fluorocarbon product from any undesired aliphatic fluorocarbon product; and
- d) recycling any undesired aliphatic fluorocarbon products to step a).

The term "aliphatic fluorocarbon" has previously been defined. The term "reactive aliphatic fluorocarbon intermediate compound" is intended to mean any aliphatic fluorocarbon, which is capable of reacting with aliphatic fluorocarbons and other reactive aliphatic fluorocarbons. This term includes species such as radicals, ions or carbenes.

DETAILED DESCRIPTION OF THE INVENTION

The new manufacturing process starts by creating reactive intermediates from a portion of the starting fluorocarbons. This is accomplished by breaking chemical bonds by the well known techniques of pyrolysis, radiation with particles, microwaves, plasmas, ultra violet light, infrared light or similar means to create radicals, ions or carbenes. These reactive intermediates then react with other reactive intermediates or with ordinary molecules making new bonds, which results in new products directly or in subsequent steps.

The generation of fluorocarbon reactive intermediates by these routes is special in that elemental fluorine is not made. This may be because of the large energy required to break the carbon-fluorine bond and the small energy gain resulting from the formation of the fluorine-fluorine bond. This peculiarity, part of the basis of this invention, of fluorocarbon reactive intermediate generation distinguishes it from hydrocarbon reactive intermediate generation in which some hydrogen and carbon are made. These two species do not react further and result in a loss of yield of desired products.

There are frequently a large variety of products made from very reactive intermediates. This is usually considered as a hindrance to successful syntheses of individual compounds. Among the products made, some are desirable and others are undesirable. This invention requires the separation of the desired products from the undesired products by distillation or other physical methods. The undesired products may then be recycled to the process to again form similar reactive intermediates, without losses of yield because of fluorine formation. Successful recycle also occurs, because of the principle of microreversibility, which requires some portion of the undesired product to revert to its starting materials under the conditions of production. These reactive intermediates from undesired products, then, with added starting material will form a mixture of products, including more of the desired products. Thus, the undesired products can be recycled endlessly and the yields of the desired products will be enhanced. By this invention even low initial yields can be converted to commercially viable processes. In some cases, where a product is unusual and highly desirable, even very low initial yields may result in commercial processes.

An example of microreversibility is shown in the Table. R 125 (see Table of Abbreviations) is made from the starting material R 133a and R 133a is made, in small yield, from R 125. Therefore, if R 125 is an undesired product, it can be recycled to the starting material as part of the yield enhancement process for the desired product.

In addition to microreversibility, there are also indirect reactions which aid the recycle of undesired products. R 125 was shown to make R 134a. In a separate experiment it was shown that TFE is made from R 134a. Thus, R 125, the undesired byproduct of TFE,

can be converted to TFE at least in two ways; by reverting to the starting material, R 133a, and via another intermediate, R 134a which also serves as a starting material for TFE.

In fluorocarbon starting materials containing hydrogen, some hydrogen fluoride may be generated. This does not represent a loss of those fluorine atoms because of the very low energy required for hydrogen fluoride to add to an olefin and reform the desired carbon to fluorine bond forming both starting materials and products. This is illustrated in the examples by the formation of R 134, presumably from TFE and hydrogen fluoride. Any hydrogen fluoride not reacting to reform carbon to fluorine bonds during the process may be recovered separately and used to form carbon-fluorine bonds either separately or by recycle.

In fluorocarbon starting materials containing hydrogen and chlorine, hydrogen chloride may be generated. This does not represent an endpoint for those atoms because in the invention the addition of hydrogen chloride to the reactants results in the formation of desired products containing chlorine.

Some of the olefinic products telomerize or polymerize under reaction conditions and these products may still contain useful carbon-fluorine bonds. The volatile telomers and polymers can be subjected to the same separation and recycle steps as other volatile byproducts. The less volatile telomers and polymers would require mechanical harvesting and special handling but in theory all products containing carbon-fluorine bonds may be recycled to extinction to improve the yields.

The choice of which are the desired products and undesired products is completely dependent on commercial needs at the time. Anyone skilled in the art will appreciate that a

reversal in the choice of the "desired" and "undesired" products among the fluorocarbons can be made and the process of the invention will still proceed to give good yields of the newly determined desired products.

This method of recycling to extinction has still another advantage. It provides a method for more complete use of starting materials and reduces the production of waste products. Waste products normally have to be treated in special ways to keep them from entering the environment. In this invention the need and expense for such treatments would be eliminated or much reduced.

The present invention involves the discovery of new methods for preparing fluorocarbons, and some surprising products resulting from these methods. The present invention also involves the discovery that reactive fluorocarbon intermediates are quite different from reactive hydrocarbon intermediates and how these differences can be manipulated so as to lead to increased yields of desired products.

In a first preferred embodiment, the invention relates to the production of aliphatic fluorocarbons comprising a process for generating reactive aliphatic fluorocarbon intermediates, forming new products, separating the desired products and recycling the undesired products to extinction to improve the yield of desired products.

In a second preferred embodiment, the reactive intermediates are generated by pyrolyses of aliphatic fluorocarbons.

In a third preferred embodiment, the invention relates to a process for preparing TFE in greater than 50% yield comprising pyrolyzing R 133a at a temperature below about 725°C.

In a fourth preferred embodiment, the invention relates to a process for preparing PFP comprising pyrolyzing R 133a in the presence of R 22.

In a fifth preferred embodiment, the invention relates to a process for preparing OFB comprising pyrolyzing R 124.

In a sixth preferred embodiment, the invention relates to a process for preparing CDFE comprising pyrolyzing R 133a.

In a seventh preferred embodiment, the invention relates to a process for preparing DCDFE comprising pyrolyzing R 133a in the presence of R 22 and hydrogen chloride.

In an eighth preferred embodiment, the invention relates to a process for preparing OFB comprising pyrolyzing R 125.

In a ninth preferred embodiment, the invention relates to a process for preparing R 134a comprising pyrolyzing R 125.

In a tenth preferred embodiment, the invention relates to a process for preparing R 114a comprising pyrolyzing R 124.

In an eleventh preferred embodiment, the invention relates to a process for preparing PFB comprising pyrolyzing R 125.

In a twelfth preferred embodiment, the invention relates to a process for preparing R 125 comprising pyrolyzing R 133a.

Of all the methods available to form the reactive intermediates such as carbenes, radicals and ions, pyrolysis was chosen for the instant examples. However, any of the described methods could have been used, and involve techniques already well known to persons skilled in the art.

Pyrolyses of chemical compounds are usually performed under a variety of conditions at high temperatures with a variety of residence times, with or without diluents. The pyrolyses may be performed under either batch or continuous conditions. Using continuous conditions, reaction tubes may be constructed of a variety of materials including quartz, alumina, Inconel or Monel. The tubes used in the instant examples had 1" outside diameters with the exception of the alumina tubes which were 3/8". The various tubes were placed in a 12" electrically heated furnace, which delineated the effective reaction zone. The temperatures were determined by a thermocouple in a thermowell centered in the tube. In the 3/8" alumina tube the temperature was measured external to the tube at the center point.

Each reagent was fed into the tube through its own calibrated 1/16" or 1/8" glass rotometer. The other end of the reactor was sometimes restricted to achieve the desired reactor pressure. Increasing the pressure results in increased conversions, but decreases the yield.

Residence times can be used to determine conversions, which then affect yields. Usually very low residence times with very low conversions give the best yields, but that may be commercially impractical. The residence times used varied from fractions of a second to about 30 seconds. The preferred residence time range is dictated by experience in each mixture of reactants. Higher pressures may be dictated by operating factors. The problems associated with pressure may be mitigated by reducing the residence times.

Feed rates of the reactants are, of course, a function of the size of the reacting zone. For the equipment described here the feed rates used for each reactant varied from about 0.018 moles per hour to about 4 moles per hour. Rates of about 10 moles per hour could also be used in the described reactors, but conversions would be quite low.

Inert diluents were also used to change the residence time of the reactants in the reaction zone. Inert diluents can be materials such as nitrogen, the noble gases, perfluoroalkanes and water vapor. The use of an easily condensable inert diluent would result in easier separation of the products from a large volume of diluent.

A literature reference pertinent to this invention is by Robert P. Salmon and Edward R. Ritter in "Experimental Flow Tube Study on Pyrolysis of 2-Chloro-1,1,1-Trifluoroethane," Chem. Phys. Processes Combust., 1996, pages 507-510. Salmon et al. report on the pyrolysis of a mixture of 2% 2-chloro-1,1,1-trifluoroethane, [R 133a], and 98% nitrogen in a quartz flow tube reactor at atmospheric pressure over a temperature range from 700°C to 875°C. At temperatures below 777°C, trifluoroethylene, [TFE], was the most abundant product, and other products formed included 1,1,1,4,4,4-hexafluoro-2-butene,

[HFB], and 2-chloro-1,1-difluoroethylene, [CDFE]. However, below about 725°C, TFE was not formed to any extent. At higher temperatures, the yield of TFE drops sharply, while the yield of 1,1,1,3,3-pentafluoropropene, [PFP], increases steadily. Other products formed at high temperature include 1,1,1-trifluoro-2-propyne.

Experimenting with temperature ranges, residence times, dilution and reactant combinations has now led to the discovery of many results not described in the literature. One surprising result observed was that by introducing additional chemicals still other products can be made in good yields. The results are disclosed in the Table and described below. The yields given are steady state values and do not reflect the ultimate values to be derived from recycle to extinction.

Starting with R 133a under selected pyrolytic conditions, (Runs 1-3), TFE can be made in yields exceeding 50%, contrary to any expectation from the work of Salmon et al.

When the same reactant, R 133a, is pyrolyzed at about 700°C and less than 10% conversion, (Run 4), CDFE becomes the important product in good yields. This is unexpected in face of the Salmon and Ritter reference which states that CDFE should be formed only at higher temperatures.

It has also been discovered that TFE can also be made in good yields from R 134a, (Run 15).

Salmon and Ritter report that PFP does not appear as a product of the pyrolysis of R 133a until about 750°C or higher temperatures are used and even then only poor yields

were made until temperatures over 800°C. It has now been discovered that by the addition of R 22 to the R 133a, (Runs 6-9), PFP can be made in good yields at temperatures of 725–750°C.

In a very unusual case, DCDFE can be prepared by performing the same pyrolysis in the presence of hydrogen chloride (Run 10). Hydrogen chloride would not be expected to take part in reactions of this sort.

From either R 124 (Runs 11 and 12) or R 125 (Runs 13 and 14) good yields of OFB can be made. R 125 also makes PFB and R 124 also makes R 114a.

The pyrolysis of R 133a almost always generates R 125 (Runs 2 and 5). The pyrolysis of R 125 (Run 14) produces R 134a, which in turn, produces TFE (Run 15).

It will be appreciated that the instant specification and claims are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

TABLE OF ABBREVIATIONS

CDFE = 1-chloro-2,2-difluoroethylene
DCDFE = 1,1-dichloro-2,2-difluoroethylene
HFB = 1,1,1,4,4,4-hexafluoro-2-butene
OFB = 1,1,1,2,3,4,4,4-octafluoro-2-butene
PFB = perfluorobutane
PFP = 1,1,1,3,3-pentafluoropropylene
R 114a = 1,1-dichloro-1,2,2,2-tetrafluoroethane
R 12 = dichlorodifluoromethane
R 123 = 1,1-dichloro-2,2,2-trifluoroethane
R 124 = 1-chloro-1,2,2,2-tetrafluoroethane
R 125 = 1,1,2,2,2-pentafluoroethane
R 13 = chlorotrifluoromethane
R 133a = 1-chloro-2,2,2-trifluoroethane
R 134 = 1,1,2,2-tetrafluoroethane
R 134a = 1,2,2,2-tetrafluoroethane
R 22 = chlorodifluoromethane
TEFE = tetrafluoroethylene
TFE = trifluoroethylene

Run	Reactants[a]	Conditions[b] T/RT/Tube	Moles Fed/hr	Moles/100g Fed	Consumed		Moles Consumed or Made/100g Fed		% Yield	
					A	B	Product C[c]	Product D[c]	Product C	Product D
	A/B			A/B			Product C[c]	Product D[c]	Product C	Product D
1	R 133a	725/26/Q [2% in N2]	0.018	0.844	0.494		TFE/0.398		80.6	
2	R 133a	725/26/Q [10% in N2]	0.088	0.844	0.267		TFE/0.182	HFB/0.051	68.1	R 125
3	R 133a	725/3.6/A [20% in N2]	0.177	0.844	0.128		TFE/0.074		58.1	
4	R 133a	700/3.6/A [20% in N2]	0.177	0.844	0.071		CDFE/0.061		85.8	
5	R 133a	723-774/50/I	0.372	0.844	0.684		TFE/0.037	R 125/0.208	5.3	HFB, R 123
6	R 133a/R 22	725/26/Q	0.088/0.088	0.488/0.488	0.345	0.443	TFE/0.084	PFP/0.335	10.6	42.5
7	R 133a/R 22	750/26/Q	0.088/0.097	0.468/0.515	0.438	0.485	PFP/0.371		40.2	
8	R 133a/R 22	730/26/Q	0.088/0.097	0.468/0.515	0.341	0.457	PFP/0.318		39.8	
9	R 133a/R 22	725/26/Q	0.088/0.097	0.468/0.515	0.316	0.446	PFP/0.295		38.8	
10	R 133a/R 22	745/26/I [in HCl atm.]	0.044/0.044	0.488/0.488	0.378	0.326	DCDFE/0.128	R 12&13/0.107	18.2	15.2
11	R 124	700/3.6/A	0.885	0.733	0.228		OFB/0.065	R 114a/0.05	28.5	R 133a
12	R 124	715/3.6/A	0.885	0.733	0.357		OFB/0.14	R 114a/0.06	39.2	16.8
13	R 125	800/3.6/A	0.885	0.833	0.286		OFB/0.099	PFB/0.021	34.6	7.3
14	R 125	840/0.9/A	3.688	0.833	0.178		OFB/0.054	R 134a/0.049	39.7	23.1
15	R 134a	870/0.9/M	3.688	0.98	0.076		TFE/0.04	TeFE/0.013	52.6	17.1

[a]:	R 124 = 1-chloro-1,2,2,2-tetrafluoroethane	[c]:	CDFE = 1-chloro-2,2-difluoroethylene
	R 125 = 1,1,2,2,2-pentafluoroethane		DCDFE = 1,1-dichloro-2,2-difluoroethylene
	R 133a = 1-chloro-2,2,2-trifluoroethane		HFB = 1,1,1,4,4,4-hexafluoro-2-butene
	R 134a = 1,2,2,2-tetrafluoroethane		OFB = 1,1,1,2,3,4,4-octafluoro-2-butene
	R 22 = chlorodifluoromethane		PFB = perfluorobutane
[b]:	T/RT/Tube:		PFP = 1,1,1,3,3-pentafluoropropylene
	T = Temperature in Centigrade		R 114a = 1,1-dichloro-1,2,2,2-tetrafluoroethane
	RT = Residence Time in seconds		R 12 = dichlorodifluoromethane
	Tube = Tube constructed of:		R 123 = 1,1-dichloro-2,2,2-trifluoroethane
	A = Alumina; I = Inconel; M = Monel; Q = Quartz		R 13 = chlorotrifluoromethane
			R 134 = 1,1,2,2-tetrafluoroethane
			TeFE = tetrafluoroethylene
			TFE = trifluoroethylene
			Other abbreviations in footnote[a]

TABLE